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Research and Preparation Method of Flexible Tactile Sensor Material

Ying Huang, Min Wang, Huaili Qiu, Bei Xiang and Yugang Zhang
Hefei University of Technology
Hefei, Anhui,
China

1. Introduction

A kind of new material suitable for flexible tactile sensor and its preparation method will be introduced. The tactile sensor applied this new material and method can be used in many kinds of occasions which contacting pressure measurement such as humanoid robot sensitive skin, medicine and so on.

This material is composite of carbon black and silicone rubber filled nano-SiO₂ as the main raw material, with a view to obtain sensitive material of flexible tactile sensor with both flexibility and tactile function.

In this chapter, based on the new flexible tactile sensor material, the effect that the material filled nano-SiO₂ has made to electrical and mechanical performance of pressure sensitive conductive rubber is investigated so as to theoretically analyze the property of nano-SiO₂ and the mechanism of modified by nano-SiO₂. Meanwhile, through the experiments of doping nano-particles into the flexible tactile sensor sensitive materials, the effect of nano-SiO₂ on the conductivity, resistance creep behavior and temperature stability of the sensitive materials were researched, as well as analyses are made on improving linearity, hysteresis and repeatability of tactile sensor. Moreover, the performance comparison produced by filled different content nano-SiO₂ and unfilled nano-SiO₂ into the new flexible tactile sensor material. Thereby, the optimum filled weight percent of nano-SiO₂ was obtained. The results showed that nano-SiO₂ has good modified role for flexible tactile sensor.

The preparation method will be used liquid silicone rubber solution blending molding. At room temperature and under normal pressure, the pressure sensitive liquid silicone rubber solution is filled into the arbitrary tactile sensor structure model and cured into molding. This method is suitable for various structures of the tactile sensor array.

2. Major raw materials and preparation methods

2.1 The main raw materials:

- GD-401 single component room temperature vulcanization silicon rubber;
- ECP-CB-1 high-conductive carbon black, with resistivity of 0.2 ~ 0.6 Ω·cm, average particle diameter is 30-40nm, specific surface area is 1000-1100 m² /g;
- Nano-SiO₂, with particle diameter of 15 ~ 20 nm;
- Si-69 silane coupling agent, with density of 650 ~ 750 kg/m³.

Source: Sensors, Focus on Tactile, Force and Stress Sensors, Book edited by: Jose Gerardo Rocha and Senentxu Lanceros-Mendez, ISBN 978-953-7619-31-2, pp. 444, December 2008, I-Tech, Vienna, Austria

2.2 Sample preparation:

The preparation of laboratory samples adopts solution blending method.

2.2.1 Preparation of samples of experiment of conductive mechanism

At normal temperature and pressure, adding high-conductive carbon black ECP-CB-1 to liquid silicone rubber, a mixed solution is prepared by ultrasonic dispersion for 30 to 40 minutes with FS-150 ultrasonic disposal equipment. Injecting the mixed solution to the structural model of tactile sensor, it is molded at room temperature with time of 64 ~ 72 hours.

2.2.2 Preparation of samples of experiment of nano-modification

At normal temperature and pressure, mixing high-conductive carbon black ECP-CB-1 and Si-69 silane coupling agent, the mixed solution A is prepared by ultrasonic dispersion for 30 to 40 minutes with FS-150 ultrasonic disposal equipment. Adding nano-SiO₂ powder to mixed solution A, mixed solution B is prepared by ultrasonic dispersion for 30 to 40 minutes. Adding the mixed solution B to the liquid silicone rubber, the mixed solution C is prepared by ultrasonic dispersion for 20 to 30 minutes. Injecting the mixed solution C to the structural model of tactile sensor, it is molded at room temperature with time of 64 ~ 72 hours.

2.3 Sample components

Samples	S1	S2	S3	S4	S5	S6	S7	S8
ECP/RTV	4%	6%	8%	10%	12%	14%	16%	18%
Igp	8.66	7.1	4.42	3.05	3.01	2.83	2.45	2.44
Region	A	B					C	

Table 1. Components of samples of experiment for conductive mechanism

Samples	A1	A2	A3	A4
ECP/RTV	8%	8%	8%	8%
SiO ₂ /RTV	0%	1%	3%	5%

Table 2. Components of samples of experiment for nano-modification

3. Fundamental theories

3.1 Conductive mechanism of the pressure-sensitive conductive composites

The new pressure-sensitive conductive composite is mainly composed by adding the carbon black of the compound silicon rubber and its conductive characteristics is closely relate to carbon black content added into the matrix material. Along with the increase of the carbon black content of the composite, the conductivity of the material slowly rises. When volume fraction of the carbon black particle reaches certain critical value, the volume resistivity of the composite sharply declines shown as Fig.1. Such sharp transition area from the high resistivity to the low resistivity is known as percolation zone, and this critical value is called as percolation threshold value. McLachlan and other people combined the effective

medium conductive model and the percolation model, put forward the universal General Effective Media (GEM) which could explain the conductive characteristics of the carbon black filled composite as follows[1]:

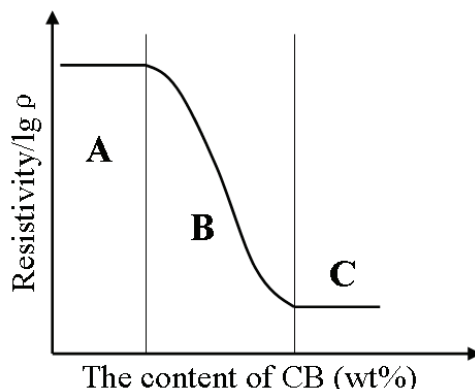


Fig. 1. Change of the resistivity along with carbon black contents

$$\frac{(1-\phi)(\sigma_1^{1/t} - \sigma_m^{1/t})}{\sigma_1^{1/t} + \{(1-\phi_c)/\phi_c\}\sigma_m^{1/t}} + \frac{\phi(\sigma_h^{1/t} - \sigma_m^{1/t})}{\sigma_h^{1/t} + \{(1-\phi_c)/\phi_c\}\sigma_m^{1/t}} = 0 \tag{1}$$

In (1): ϕ is the volume fraction of the conductive particle in composite; ϕ_c is the critical volume fraction of the conductive filler when the percolation passage is formed, which is also known as critical percolation threshold value; σ_1 is the matrix's conductivity; σ_h is the conductivity of the conductive particle; σ_m is the composite's conductivity; t is the percolation coefficient of the composite. As for carbon black filled conductive silicon rubber, carbon black conductivity is far larger than conductivity of the silicon rubber, therefore the conductivity of the polymeric matrix could be approximately considered as zero, namely $\sigma_1 = 0$, $\rho_m = 1/\sigma_m$, $\rho_1 = 1/\sigma_h$, Then (1) could be simplified as:

$$\rho_m = \rho_1 \left(\frac{1-\phi_c}{\phi-\phi_c} \right)^t \tag{2}$$

In the (2): ρ_m is the volume resistivity of carbon black filled conductive composite; ρ_1 is the carbon black's volume resistivity. Things requires attention is that (2) only applicable to condition when the volume fraction of the carbon black particle is close to critical threshold value ϕ_c .

Effective medium model describes the phenomenon of composite conductivity change along with the carbon black content, but does not explain the conductive reason from the microscopic structure of the conductive particle, fails to reveal the essential conductive mechanism of the pressure-sensitive composite. Currently researches on the explanation of the conductive mechanism are too much, but none of them has a unified theory [2]. Summary of the main conductive mechanism has two versions: Conductive path theory and quantum tunnel effect theory. Conductive path theory is the model theory only on the foundation of macro test feature instead of discussing the micro electronic movement within

the material, is the modeling of the experiment phenomenon. It believes that conductive theory of the composite is due to the mutual contact of the filled carbon black particle, form conductive link inside of the silicon rubber, but this theory could not explain the problem that when filled less carbon black particle, the composite still possesses conductivity. Quantum tunnel effect theory is put forward by Sheng.P and other peoples on the foundation of the quantum tunnel effect theory, which tries to explain from the micro electronic movement in the material [3, 4]. Suppose the statistic average value of the conductive particle space is ω , relationship between the macro current density showed $J(\varepsilon)$ and ω is:

$$J(\varepsilon) = J_0 \exp\left[-(\pi\chi\omega/2)(\varepsilon/\varepsilon_0 - 1)^2\right] \quad (3)$$

In the equation, ε_0 is the field between spaces without external forces, ε is the field between spaces when giving external forces, $\chi = \sqrt{2mV_0/\hbar^2}$, m is the electronic mass, \hbar is the reduced Planck constant, and V_0 is the barrier height.

This theory could explain the electronic transition pattern of the carbon black particle before direct contact within the material, which as a result explains in the sense the real reason for conduction of the composite when with less carbon black particle content. But this theory also could not unify the conductive mechanism of the composite with the different carbon black filled content, which needs to be continuously researched in the future. Currently the better explanation for the conductive mechanism for different carbon black filled content is to combine the conductive path theory and quantum tunnel effect theory. Simultaneous function of the two theories is as shown in Fig. 2. From the microscopic structure sketch of the carbon black particle filled silicon rubber, it could be found that carbon black particle structure in the silicon rubber is not evenly dispersed, instead of forming several congeries, which has spaces between each other. Carbon black particles in the congeries are mutually contacted, whereas conduction between congeries is caused by the electronic transition of the nearest carbon black particles.

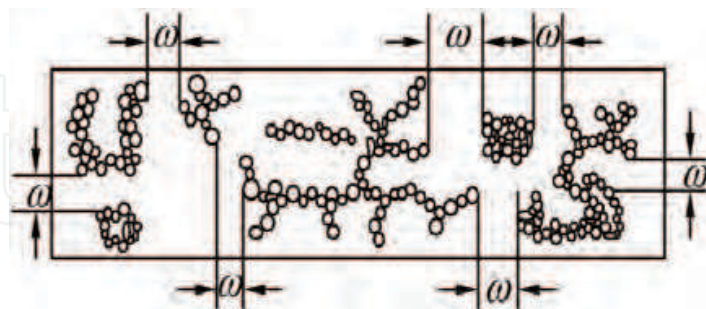


Fig. 2. Structural of the carbon black particle in the pressure-sensitive composite

Conductive characteristics curve of the composite is divided into three areas [5] (shown in Fig.1). A zone with higher resistivity is called as insulation zone; B zone with sharply decreased resistivity is called as percolation zone; stabilized C zone with lower resistivity is called as conductive zone. A zone: insulation zone, when carbon black content in silicon rubber is lower than the percolation threshold value, space between carbon black particles is large, the gathering of the carbon black particle is few, so the conductive path is hard to

form; space between congeries is large, the electronics between particles is hard to generate transition, then the composite shows the high resistivity; usually resistivity is higher than $10^{10}\Omega \cdot \text{cm}$. B zone: percolation zone, along with continuous increase of the carbon black contents in the conductive silicon rubber, carbon black particle gathers link, starts forming conductive path; space between congeries continuously decrease, two adjacent particle distance decrease to 1.5-10nm. Probability of the electronic transition raise greatly, as a result sharply increase the conductivity of the composite. C zone: conductive zone, along with the continuous increase of the carbon black filled, carbon black content would exceed percolation threshold value, the space between carbon black particles also would further shorten(it is generally agreed to be 0.35-1.5nm); congeries link gradually stabilizes, the quantity of conductive path basically reach the maximum value. Along with further shortening of the neighboring carbon black particle space, when particle distance is smaller than 0.35nm, it is assumed that contact between the particles could be approximately regarded as pure particle contact, in addition current and voltage show the linear relationship, show the obvious Ohm characteristics.

Summarize the above discussion, composite resistivity in the percolation zone has the maximal change along with different carbon black content. Elastic deformation of the pressure-sensitive composite under the external forces would lead volume fraction variance of the carbon black [6], consequently result in variation of the composite conductivity, which exactly satisfies the design requirement of the tactile sensor, therefore research on the conductive characteristics of the flexible tactile sensing material in this paper is mainly in the percolation zone, and gives priority to quantum tunnel effect theory.

3.2 Piezoresistive effect

Resistance of the pressure-sensitive composite shows the regular variation under the pressure, which possesses good piezoresistive characteristics, could establish piezoresistive characteristics model of the pressure-sensitive composite based on quantum tunnel effect theory. On the assumption that initial thickness of the conductive composite is h_0 , initial resistance value is R_0 , k_1 is the elastic coefficient of the silicon rubber matrix. When pressure-sensitive composite is under pressure F , the material thickness is h , then within the elastic deformation there is:

$$F = k_1(h_0 - h) \quad (4)$$

Secondly, suppose ω is directly proportional to h , proportion coefficient is k_2 namely:

$$\omega = k_2 h \quad (5)$$

Electric field \mathcal{E} between spaces is inverse proportional when other condition unchanged:

$$\mathcal{E} / \mathcal{E}_0 = \omega_0 / \omega = h_0 / h \quad (6)$$

According to Ohm's law, bring the (3) ~ (6) to the resistance equation, then deduce the relationship of resistance value change along with external forces:

$$\begin{aligned}
 R(F) &= h/\sigma s = Jh/ES \\
 &= \left(\frac{h_0 k_1 - F}{\sigma_0 S k_1} \right) \left(\exp \left(\frac{\pi \chi k_2 F^2}{2 k_1 (h_0 k_1 - F)} \right) \right) \\
 &\approx \left(\frac{h_0 k_1 - F}{\sigma_0 S k_1} \right) \left[1 + \frac{\pi \chi k_2 F^2}{2 k_1 (h_0 k_1 - F)} + \frac{\pi^2 \chi^2 k_2^2 F^4}{8 k_1^2 (h_0 k_1 - F)^2} + \dots \right] \\
 &= R_0 - \frac{R_0}{k_1 h_0} \cdot F + \frac{\pi \chi k_2 R_0}{2 k_1^2 h_0} \cdot F^2 + \frac{\pi^2 \chi^2 k_2^2 R_0}{8 k_1^3 h_0 (h_0 k_1 - F)} \cdot F^4 + \dots
 \end{aligned} \quad (7)$$

It is accurate to quadratic term generally, therefore:

$$R(F) = R_0 - AF + BF^2 \quad (8)$$

Among this, $A = R_0/k_1 h_0$, $B = (\pi \chi k_2 R_0)/(2 h_0 k_1^2)$, above equation reflects the functional relationship that the conductivity of pressure-sensitive conductive silicon rubber changes along with external force variation; calculate the value of A and B by least-squares method according to test data $R(F) \sim F$ and (8).

3.3 Influencing mechanism of the temperature to conductivity

Because influence of the temperature to matrix material is considerable, hence changes the conductivity of the pressure-sensitive conductive composite, so research on the influence of the temperature to composite conductivity is necessary. Research on the temperature characteristics for the pressure-sensitive conductive composite would mainly gain two properties: positive temperature coefficient characteristics (PTC) and negative temperature coefficient characteristics (NTC). From the discussion of the temperature characteristics of the pressure-sensitive conductive silicon rubber on conductive mechanism will find it is possible that these two properties appear in one sample heating process [7].

According to quantum tunnel effect theory by Sheng P and others, use ε_T to represent the electric field change caused by the thermal disturbance when heating up, ε_A represents the extra electric field, then:

$$\varepsilon = \varepsilon_T + \varepsilon_A \quad (9)$$

When extra electric field ε_A is very low, namely when $\varepsilon_A < \varepsilon_T$, then the actual tunnel current is:

$$\Delta J = J(\varepsilon_A + \varepsilon_T) - J(\varepsilon_A - \varepsilon_T) \quad (10)$$

Here use the equation below to define $\Sigma(\varepsilon_T)$:

$$\Sigma(\varepsilon_T) = \frac{\Delta J}{\varepsilon_A} = 2 \frac{dJ(\varepsilon_T)}{d\varepsilon_T} \quad (11)$$

Average is obtained as the equation below:

$$\sigma = \int_0^{\infty} P(\varepsilon_T) \Sigma(\varepsilon_T) d\varepsilon_T \quad (12)$$

In it: $P(\varepsilon_T) = \kappa \exp\left(-\frac{\omega A \varepsilon_T}{8\pi \kappa T^2}\right)$ represents the appearing probability for ε_T .

Whereas fundamental equation of the quantum tunnel effect theory is (3)
Bring the (3) and (10) to the (11); ultimately get the following equation:

$$\sigma = \sigma_0 \exp \left[\frac{-A\varepsilon_0^2 \omega}{8\pi\kappa} \right] \left[T + \frac{A\varepsilon_0^2}{4\pi^2 \chi\kappa} \right] \quad (13)$$

In the equation: $\chi = \sqrt{2mV_0/\hbar^2}$, whereas κ is Boltzmann constant, m is the electronic mass, e is the electron charge, V_0 is the barrier height, A is carbon black particle space areas of the capacitance, they are all the constant. There are only two variants ω and T .

$$M = A\varepsilon_0^2 / 8\pi\kappa, \quad N = A\varepsilon_0^2 / 4\pi^2 \chi\kappa$$

Then (13) becomes:

$$\rho = \rho_0 \exp[M \omega / (T + N)] \quad (14)$$

It could be found from the above equation that conductivity is related to temperature T and ω ; ρ decreases along with the increase of T and increases along with the increase of the ω . Regularity could be summarized as when temperature of the pressure-sensitive conductive composite increases, silicon rubber matrix generates thermal expansion that results in space ω expansion and raise the resistivity; whereas temperature rise also raise the electronic transition probability between the carbon black particles (namely thermal disturbance) that results in fall of the resistivity. It could be said that resistivity changes along with the temperature mainly subject to the two kind functions of the thermal expansion and thermal disturbance, and the characteristics showed mainly depends on which takes the leading role. If thermal expansion takes the leading role, and then PTC characteristics appears, if thermal disturbance takes the leading role, then NTC characteristics appears.

4. Study and analysis of piezoresistive and temperature properties

In the above, we have put forward the mechanism of piezoresistive characteristics and temperature properties of flexible tactile sensor material, and in the following, we will analyze its piezoresistive characteristics and temperature characteristics related with the experiment result.

4.1 Piezoresistive effect experiment and result analysis

Piezoresistive effect experiment is intended to test the relationship between pressure and resistance, hence to further analyze the conductivity of the pressure-sensitive conductive composite under pressure, which adopt the measuring method as shown in Fig.3. Among it the upper and lower pole are circular copper poles, and sample and pole are bonded by conductive silver adhesive in order to guarantee good metallic connection. Piezoresistive experiment respectively for sample S3, S4 and S5, records are drawn into curve as shown in Fig.4.

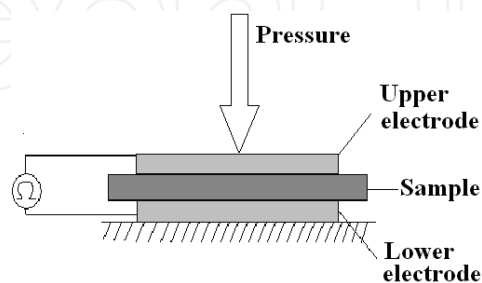


Fig. 3. Piezoresistive effects measuring device

Fig.4 reflects the relationship of the pressure-sensitive conductive composites' resistivity changing along with pressure. According to (8) based on experiment curve, we could fit the value A, B each parameter value of three samples is shown as Table 3.

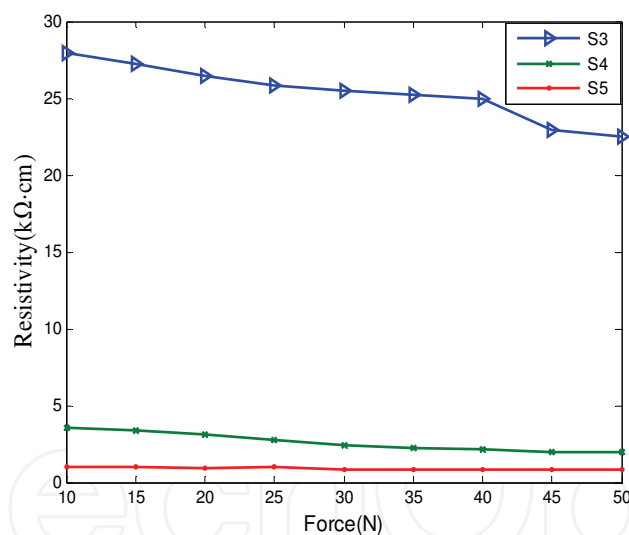


Fig. 4. Piezoresistive characteristics with different carbon black content

Parameters	$A(\Omega/N)$	$B(\Omega/N)$	$R_0(\Omega)$
Sample s3	11.518	0.9288	915.33
Sample s4	13.573	0.6572	132.27
Sample s5	1.7962	0.0909	35.777

Table 3. Parameters estimated value of the three samples

It is observed from Table 3 that B value decreases along with the increase of the carbon-black content, the linearity of the sample piezoresistive characteristics would be better,

which also provides reference for this material satisfying the design requirement of the flexible tactile sensor. The value ω can be estimated from the value of A and B , but is inconsistent with the theoretical value. The reason may be due to the simplified model which did not consider the microscopic structure of carbon black particles. Carbon black particles are not uniform distribution in the matrix material, but uneven distribution.

4.2 Temperature characteristics experiment and result analysis

Place the sample into the high and low temperature experiment box with the model number of GDW-100 produced by Sunan Laboratory Apparatus Factory, introduce conductor through electrode, measure resistance with Ohmmeter, respectively take temperature test to sample S3, S4, S5, heat from 30°C to 90°C, record 20 minutes constant temperature after heating 10°C, gain resistance temperature characteristics of the pressure-sensitive conductive rubber with different carbon black content that is shown in Fig.5.

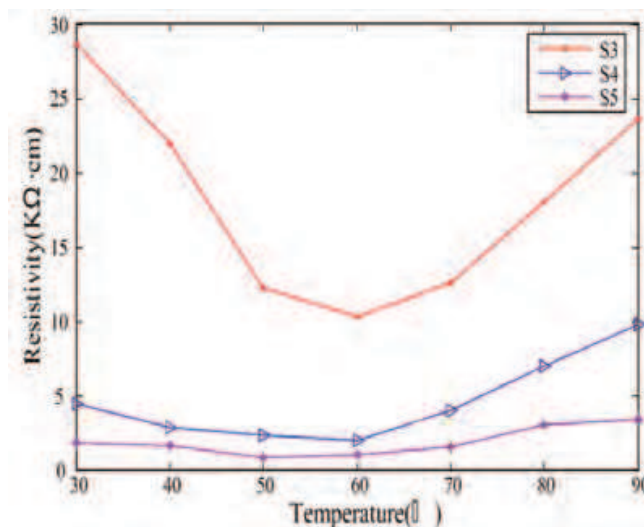


Fig. 5. The resistivity temperature characteristics with different carbon black content

In Fig.5, resistivity of sample S3, S4, S5 all have the phenomenon of continuously rise after decreasing. Major analysis is in the percolation zone, temperature's influence to quantum tunnel effect is comparatively apparent when heating freshly, which means the thermal disturbance takes leading role, then the sample resistivity appears the downward trend, shows the negative temperature coefficient. After temperature reaching certain value, quantum tunnel effect is stabilized, whereas different thermal expansion rates of the carbon black particle and silicon rubber result in the enlarged space of the carbon black particle. Sample resistivity increases, which means the thermal expansion takes leading role, shows the positive temperature coefficient characteristics.

It could also be discovered from Fig.5 that along with increase of the carbon black content, resistivity of the pressure-sensitive conductive rubber decreases; furthermore temperature stability is also better. This is because along with the increase of the carbon black content, average space between carbon black particles become smaller, quantum tunnel effect is increasingly obvious, resistivity value continuously falls. But increase of the carbon black content stabilizes the quantum tunnel effect, reduces influence of the thermal disturbance, whereas combined function of thermal disturbance and thermal expansion stabilize the sample resistivity temperature characteristics much more.

As materials of the flexible tactile sensing, temperature stability influences its operating temperature range. In order to increase the temperature stability of such material, several literatures put forward the way of adding other filled materials such as graphite particle and nanometer particles etc [8].

5. Nano-modification technology of flexible tactile sensor material

5.1 Characteristics and modification mechanism of nanomaterials

Because of high relevance of quantum mechanics, nanomaterials show their different properties from macro and micro's. In the field of polymer materials modification study, the nanoparticles have been considered to be good filling material to improve the mechanical and physical characteristics of high molecular polymer. The specific surface area as huge as $1000\text{m}^2/\text{g}$ at nanometer level and its unique performance have aroused extensive research in various fields of natural sciences and engineering sciences.

In the process of mixing nano powder and high molecular polymer, agglomerate will be broken, and then become nanoparticles chain. Through study, Friedlander finds that [9-10] inorganic oxide nanoparticles chain aggregates have feature of flexibility, which can lengthen under extension and the nanoparticles chain curl and reunite into agglomerate after removing tension. That is, nanoparticles chain aggregates have feature of reaggregation, which shows property of elasticity mechanics similar to polymer chains, and at the same level with ordinary high polymer molecular chain, as shown in Fig.6. Another important contribution of nanoparticles chain is three-dimensional network formed through nanoparticles chains' self-contact or by nanometer elastic layer absorbed in the surface of the polymer particles chains. The study found that network formed by nanoparticles has property of elasticity mechanics similar to polymer, which makes the particles network and polymer network extend, intervein and mix together, effectively eliminates the interfacial energy difference, and reduces stress concentration, so as to enhance the strength of high polymer complex, thereby, nanoparticles chains with flexibility have a significant impact on nano powder's dispersion and toughening in high polymer. [11].

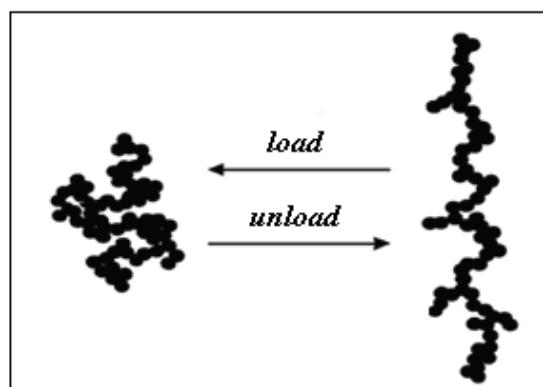


Fig. 6. Elastic behaviors of nanoparticle chain are similar to polymer chain

5.2 Test and analysis of nano composites

5.2.1 Modification of mechanical properties of sensor

In the sensors' measuring, good static and dynamic characteristics are requested, of which, linearity, repeatability and hysteresis quality is particularly important. Nano composites, as

a new type of sensor sensitive material, should also have the corresponding characteristics. The following experiment is adopted to measure the effect on the static characteristics of sensitive materials by adding different content of nano-SiO₂ or adding no nano-SiO₂. Fig. 7 shows that area of the hysteresis loop of samples A1 with no nano-SiO₂ added is far larger than that of samples A2, A3 and A4 with nano-SiO₂ added, which means that the addition of nano-SiO₂ improves the hysteresis quality of samples.

Four times loading and unloading cycle experiments are conducted in sample A1 with no Nano-SiO₂ added and sample A3 with nano-SiO₂ added, in order to test linearity and repeatability of composites used for the tactile sensor. The results in Fig. 8 show that the repeatability of sample A1 with no nano-SiO₂ added is relatively poor, but sample A3 with nano-SiO₂ added shows good repeatability in the four times experiments. This is because structure with completely different mechanical properties is formed with nano-SiO₂ added. Nano SiO₂ particles, like rigid chain, enhance the toughness and strength of polymer, change the toughness, strength and many other mechanical properties of composites [12]. Therefore, the addition of nano-SiO₂ enhances toughness, repeatability, and hysteresis of tactile sensor to different degrees.

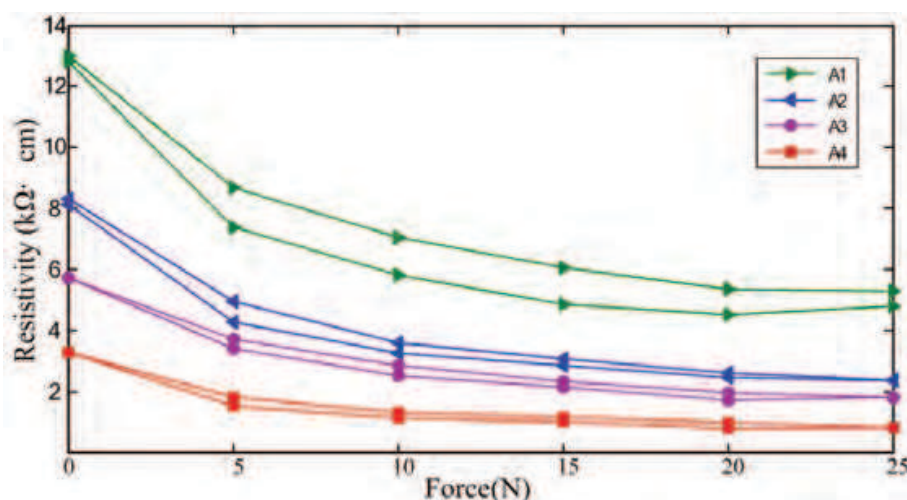


Fig. 7. Linearity and hysteresis curves

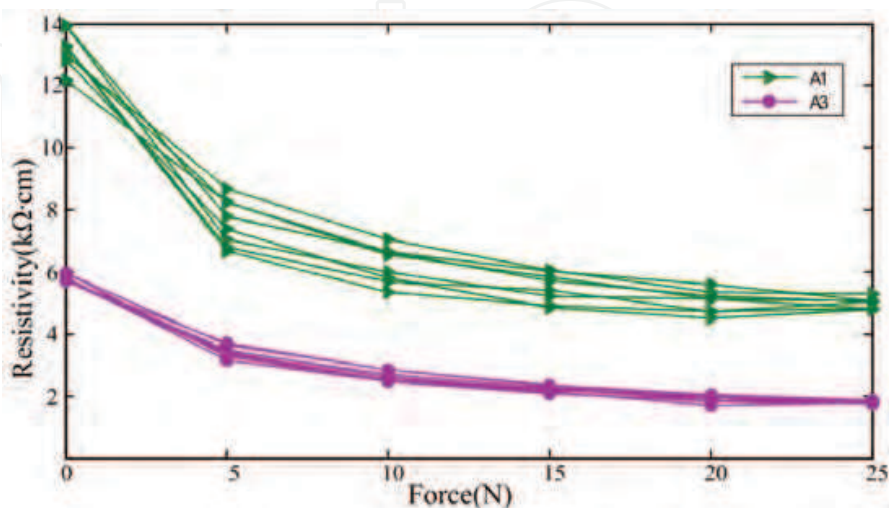
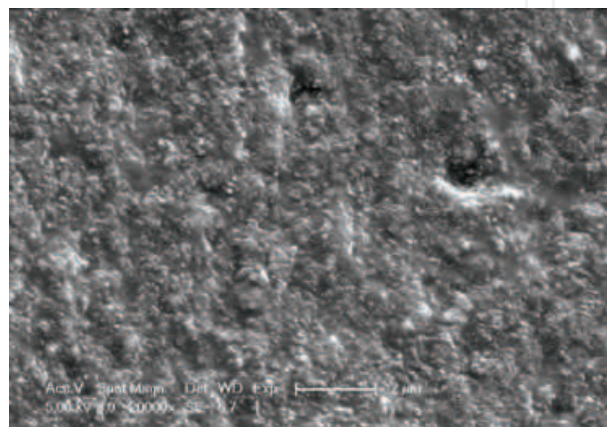


Fig. 8. Reproducibility curves

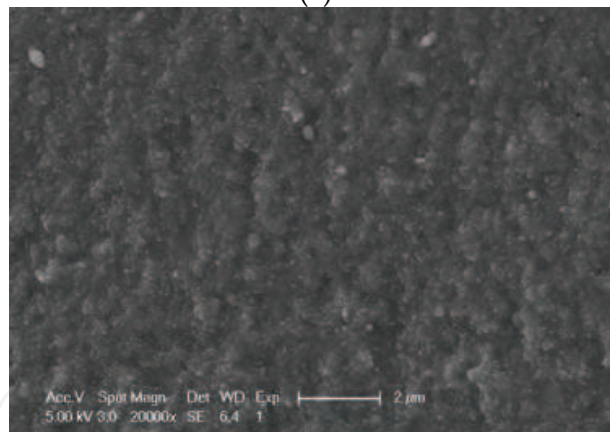
5.2.2 Characteristic of conductivity

From the experiment of mechanics above, we can also see that with the increase of nano-SiO₂ content, the resistivity of composites shows the trend of gradual decreasing. This is because when the nanoparticles and conductive carbon black are well-mixed in silane coupling agent, network formed by nanoparticles chains can effectively make particle network and polymer network extend, intervein and mix together.

Fig. 9 is the SEM image of 20000 times of sample with 3% nano-SiO₂ added and sample with no nano-SiO₂ added. In the image we can see that the addition of nano-SiO₂ significantly increases the dispersion of conductive carbon black in silicon rubber matrix, improves the uniformity of the sample, thereby increases the conductivity of the material, which is also reflected in the specific resistance in characteristic curve of the four samples in Fig. 7.



(a)



(b)

Fig. 9. Effect of 20,000 times of SEM microstructure of composites(a. no filling nano-SiO₂, b. filling nano-SiO₂)

5.2.3 Effect on resistance creep

As for sensor sensitive material, not only good piezoresistive characteristics and elastic property are required, but also good time stability. In this paper, because substrate material of the flexible sensitive composites is colloid, it shows mechanical behavior of high polymer materials, with both mechanical properties: glutinosity and elasticity. At the same time, the conductive path of the composites varies with the deformation of colloid. These phenomena are mainly embodied in the time stability of the resistance of material, such as the creep of resistance, which directly affects the sensor measurement error.

Fig.10 is the experimental results of resistance creep of sample A1 with no nano-SiO₂ added and A3 with nano-SiO₂ added under different loading. From the Figure, we can see that the relative change of specific resistance $\Delta\rho/\rho_0$ of sample A3 with nano-SiO₂ added is lower than that of sample A1, that is, the resistance creep is relatively small. Therefore, sample with nano-SiO₂ added has a better time response as tactile sensor.

Due to the addition of nano SiO₂ particles, nano SiO₂ particles, like beaded chain, strongly absorb the surrounding silicon rubber molecules with its high surface energy and surface binding energy, and create a strong chemical bonds and physical adsorption with silicone rubber molecules, thereby form a relatively complete crosslinking network structure with nano SiO₂ particle as nodes, which disperses the force to other polymer chain as common burden, prevents the rapid breakage of polymer and effectively improves the resistance creep property of composites under loading.

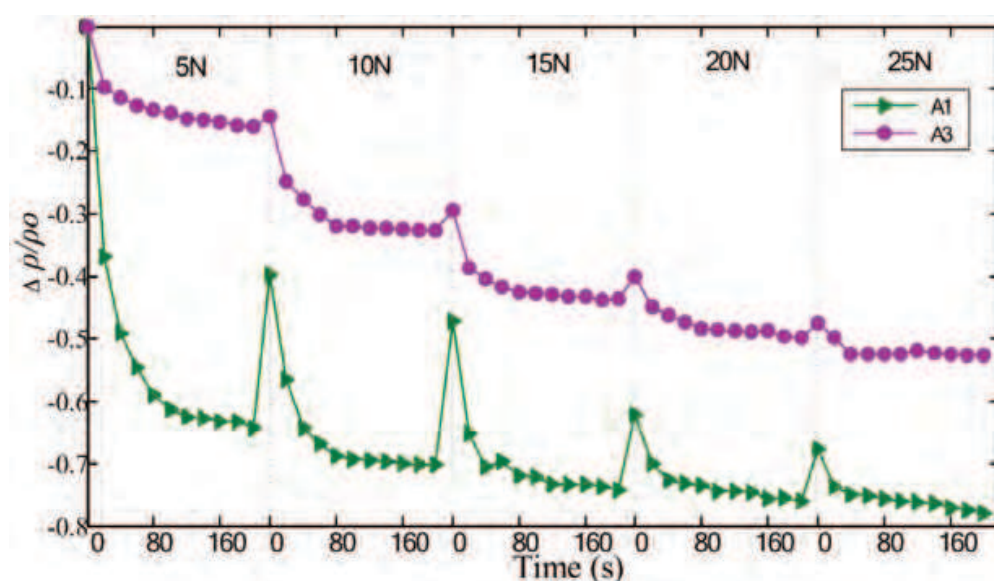


Fig. 10. Resistance creep behavior at different applied loads

5.2.4 Effect on resistance temperature properties

Resistance temperature properties of flexible tactile sensor based on the pressure-sensitive conductive rubber is effect of coactions of material's thermal disturbance and thermal expansion [8]. In the beginning of warming up, the tunnel effect is obviously influenced by temperature, that is, the thermal disturbance plays a leading role, the resistivity of the sample decreases, showing properties of negative temperature coefficient. When the temperature reaches a certain value, the tunnel effect tends to be stable. However, because the thermal expansion rate of carbon black particles and silicon rubber is different, the space between the carbon black particles increases, and the resistivity of sample increases, the thermal expansion at this time plays a leading role, showing properties of positive temperature coefficient. Refer to the Fig.11, which is the temperature experimental curve of sample A1. This phenomenon demonstrating positive and negative temperature properties and large resistance temperature coefficient is disadvantageous to the produced flexible tactile sensor.

Fig.11 shows the resistance temperature properties of samples A1, A2, A3 and A4. The resistance rate change of A2, A3 and A4 is smaller than that of A1, and the variation trend

basically shows monotonicity. We can see that the addition of nano-SiO₂ effectively improves the time stability of the samples. Further more, with the increase of the content of nano-SiO₂, the temperature stability of the samples is gradually improving, which plays an important role in the practical application and temperature properties compensation of flexible tactile sensors.

The reason of the addition nano-SiO₂ changes the temperature properties of the material is mainly related with the micro characteristics of nano-SiO₂. In the process of temperature changing, the distribution and decentralization state of filling material in the matrix decide the resistance-temperature relations. If explained in conductive pathway theory, it is because stable conductive pathway is formed, which improves the temperature stability. Therefore, the appropriate amount of nanoparticles SiO₂ prevents the agglomeration of conductive carbon black in the polymer, and plays a very good role in dispersion, which promotes the formation of a conductive circuit, and increases temperature stability and consistency of pressure-sensitive conductive rubber.

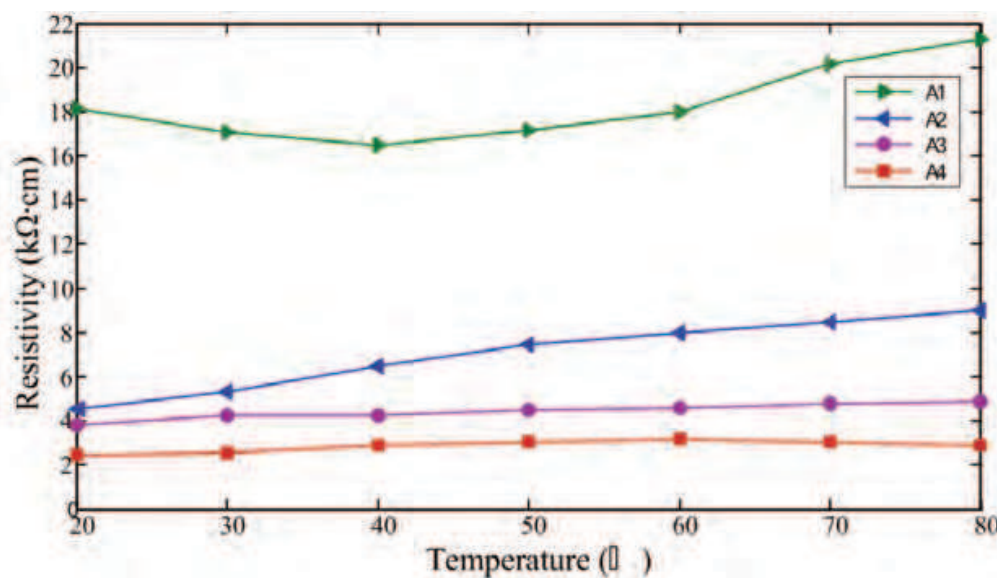


Fig. 11. The resistance temperature characteristic of with different nano-SiO₂ content

5.2.5 Performance Comparison

Of the above four samples' performance, Table 4 shows the comparison of the performance indicators of sample A1 with no nano-materials added and sample A3 with 3% nano-SiO₂ added. From Table 4 we can see that the linearity, repeatability and hysteresis as well as conductivity, resistance creep and temperature properties of sample A3 with nano-SiO₂ added have improved, of which, linearity, repeatability and hysteresis are acquired through curve fitting in the fourth loading and unloading of the above experiment. From this, we

Sample	Linearity (%)	Hysteresis (%)	Repeatability (%)	Conductivity ρ_0 (k Ω ·cm)	Creep (10N loading) $\Delta\rho/\rho_0/t$	Temperature $\Delta\rho/\rho_0/T$
A1	10.9	15.5	12.4	13.9	0.0015/s	0.00588/°C
A3	6.5	8.4	7.5	5.7	0.0009/s	0.00273/°C

Table 4. Samples A1 and A3 performance comparison

can see that all the performance of sample A3 with 3% nano-SiO₂ added have been improved, which is the best filling share. It proves that a certain content of nano materials has a modification function on flexible tactile sensor.

6. Conclusion

This paper studies conductive mechanism of the new pressure-sensitive conductive composite based on flexible tactile sensing, believes that conductive mechanism of the composite within percolation zone gives priority to quantum tunnel effect theory. Starting from the quantum tunnel effect theory it studies the relationship between pressure and resistance, and piezoresistive model could be established by using the quantum tunnel effect. Based on theory and experiment, through the analysis and research on the conductive characteristics of such new sensitive material with different content conductive fillers, the conductive mechanism could be obtained within the pressure sensitive range, which provides theoretical foundation for the study of such new flexible tactile sensing material. It also discusses the influence mechanism of the temperature to the conductivity of the pressure-sensitive conductive composite. Positive temperature coefficient (PTC) and negative temperature coefficient (NTC) characteristics of the pressure-sensitive conductive silicon rubber will appear in the heating process of one sample, which provides reference for the practical application of such new sensitive material.

Whereas there is still a certain distance between the performances of the above flexible material compared with the requirements of sensor sensitive materials, therefore, this paper further studies the modification function of nano-SiO₂ by adopting the special nature of nano materials. Since nowadays, the study on nanoparticles modified materials and nano materials' mechanical behavior is only in the early stage, which only detects the external manifestations of mechanical phenomena, far from the study on its internal mechanism [13]. Therefore, this paper mainly conducts experimental study and measurement on modification of pressure-sensitive conductive rubber after the addition of nano-SiO₂ materials. The results show that the unique properties of nano-SiO₂, the mechanical properties of pressure-sensitive conductive rubber, temperature performance and stability are significantly improved. As for the modified composites, we can improve the technical indicators of the produced tactile sensors to meet the requirement of tactile sensing. Further more, the compounding of nanoparticles and polymer modifies the heat-resistant and ageing resistance, and improves the properties of shock resistance and anti-fatigue.

Flexible tactile sensor material, presented in this chapter, has both good tactile sensing function and flexibility, its preparation method is simple. Flexible tactile sensor based on this material can measure various tactile information of contact surface, which is expected to provide a new way of thinking and research methods of the flexible tactile sensor.

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This book describes some devices that are commonly identified as tactile or force sensors. This is achieved with different degrees of detail, in a unique and actual resource, through the description of different approaches to this type of sensors. Understanding the design and the working principles of the sensors described here requires a multidisciplinary background of electrical engineering, mechanical engineering, physics, biology, etc. An attempt has been made to place side by side the most pertinent information in order to reach a more productive reading not only for professionals dedicated to the design of tactile sensors, but also for all other sensor users, as for example, in the field of robotics. The latest technologies presented in this book are more focused on information readout and processing: as new materials, micro and sub-micro sensors are available, wireless transmission and processing of the sensorial information, as well as some innovative methodologies for obtaining and interpreting tactile information are also strongly evolving.

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InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

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